Asymmetric Polymerization of Dialdehyde and Bis(allylsilane) in the Presence of Chiral (Acyloxy)borane Catalyst

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ABSTRACT: We present a study of the asymmetric polymerization of dialdehyde and bis(allylsilane) based on the enantioselective addition of allylsilane to aldehyde in the presence of chiral Lewis acid. Chiral (acyloxy)borane (CAB) derived from enantiopure tartaric acid was used as a chiral Lewis acid to promote the asymmetric polymerization. Repetitive allylation reaction between these monomers in the presence of CAB yielded optically active polymers having asymmetric carbons in their main chain. The corresponding model asymmetric reaction of β-substituted allylsilane with benzaldehyde was also studied.

Introduction

Synthesis of optically active polymers by means of asymmetric synthesis polymerization has been a topic of intense interest.[1−4] Although the synthesis of chiral polymers having one-handed helical structure has been widely studied,[5] only a few synthetic methodologies for the optically active polymers having main chain configurational chirality have been reported.[6] On the other hand, there are number of examples on asymmetric C−C bond forming reactions.[7] If these asymmetric reactions can be utilized for chiral polymer synthesis, various kinds of optically active polymers having main chain configurational chirality may be designed easily. On the basis of these considerations, recently we have performed some preliminary experiments on the asymmetric synthesis polymerization based on the repetitive C−C bond forming reactions including Diels−Alder, aldol, and allylation reaction.[8] Of these reactions, enantioselective addition of allylsilanes to aldehyde is highly promising to apply to such chiral polymer synthesis. The reaction of allyltrimethylsilane with carbonyl compounds activated by $TiCl_4$ was first reported by Hosomi and Sakurai in 1976.[9] They found that the corresponding secondary homoallylic alcohols could be obtained by this reaction in high yield. Other various kinds of Lewis acids have been introduced shortly afterward.[10] Indeed, this methodology has been widely utilized for the various kinds of organic synthesis that require C−C bond forming reaction.[11] Enantioselective addition of allylsilane to aldehyde was performed by the use of chiral Lewis acid to afford enantio-enriched homoallyl alcohols.[12] Thus, our simple idea involves that the asymmetric repetitive addition between bis(allylsilane) and dialdehyde would yield the optically active polymers having main chain configurational chirality. In this paper we have prepared new monomers for the asymmetric allylation polymerization and their polymerization to give optically active polymers.

Experimental Section

General. All reactions were carried out under an atmosphere of nitrogen. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and was freshly distilled just before use. Dichloromethane and propionitrile were distilled from calcium hydride. Both ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured on a Varian Mercury 300 spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded with a JEOL JIR-7000 FT-IR spectrometer and were reported in reciprocal centimeters (cm^{-1}). Elemental analyses were performed by the Microanalytical Center of Kyoto University. HPLC analyses were performed with a JASCO HPLC system composed of a three-line Degasser (DG-980-50), a HPLC pump (PV-980), and a column oven (CO-965) equipped with a chiral column (Chiralcel OD or Chiralpac AD, Daicel) using hexane/propan-2-ol as an eluent. A UV detector (JASCO UV-975) was used for the peak detection. Optical rotations were taken on a JASCO DIP-140 digital polarimeter using 10 cm thermostated microcell. Size exclusion chromatography (SEC) for the characterization of molecular weight and its distribution was conducted at 40 °C with a JASCO PU-980 as a pump, JASCO UVIDEC-100-III as a UV detector, and Shodex column A-802 (pore size: 20 Å) and A-803 (pore size: 100 Å) as columns. The eluent was THF, and the flow rate was 1.0 mL/min. A molecular weight calibration curve was obtained by using a series of polystyrene standards (Tosoh Co., Japan).

Monomers. Commercial samples of phthalaldehyde **(1a)**, isophthalaldehyde (**1b)**, and terephthalaldehyde (**1c)** were purified by recrystallization. Bis(2-formylphenyl) ether (**2)** was used as received. Benzaldehyde was purified by vacuum distillation on calcium hydride. Succinyl chloride (Tokyo Kasei), adipoyl chloride (Tokyo Kasei), and sebacoyl chloride (Tokyo Kasei) were used as received.

Dialdehyde (3c). The procedure is analogous to that reported in previous paper.[8c] ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.99 (s, 2H), 7.97 (d, J = 8.5 Hz, 4H), 7.26 (d, J = 8.5 Hz, 4H), 2.60 (t, J = 7.4 Hz, 4H), 1.76−1.77 (m, 4H), 1.55−1.28 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 190.8, 171.5, 155.5, 134.0, 131.2, 122.3, 109.5, 34.3, 29.0, 24.7. IR (KBr): ν (cm^{-1}) = 1756, 1690. Anal. Calcd for $C_{24}H_{26}O_6$ (410.5): C, 70.23; H, 6.38. Found: C, 70.31; H, 6.35.

Dialdehyde (4). A 200 mL round-bottomed flask was charged with 4-hydroxybenzaldehyde (2.7 g, 22 mmol) and dry DMF (80 mL). Triethylene glycol ditosylate (4.65 g, 10.1 mmol) and K_2CO_3 (3.5 g, 25 mmol) were added to the solution and heated to 100 °C for 14 h. The reaction mixture was then cooled to room temperature and poured into 1 L of water. The obtained precipitate in water was stirred for 4 h and filtered, which was recrystallized from ethanol/water (3:2). Yield: (2.46 g, 68%); mp 75−76 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.88 (s, 2H), 7.82 (d, J = 8.8 Hz, 4H), 7.01 (d, J = 8.8 Hz, 4H), 4.21 (t, J = 4.6 Hz, 4H), 3.90 (t, J = 4.6 Hz, 4H), 3.77 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 191.1, 164.1, 132.3, 130.4, 115.2, 71.3, 69.9, 68.1. IR (film): ν (cm^{-1}) = 1697, 1602, 1255. Anal. Calcd for $C_{20}H_{22}O_6$ (358.4): C, 67.03; H, 6.19. Found: C, 66.99; H, 6.15.

Bis(allylsilane) (6c). The procedure is analogous to that reported in previous paper.[8f] ^{1}H NMR (300 MHz, $CDCl_3$): δ

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(ppm) = 4.60 (s, 2H, C=CH_2), 4.52 (s, 2H, C=CH_2), 1.96 (m, 4H, =CHCH_2), 1.54 (s, 4H, −CH_2Si), 1.44 (m, 4H, =CHCH_2-CH_2), 1.31 (br s, 8H, $CH_2CH_2CH_2$), 0.01 (s, 18H, SiCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 148.2, 107.1, 38.6, 29.9, 29.8, 28.2, 27.1, −0.9. IR (film): ν (cm^{-1}) = 3037, 1633, 1249, 855. Anal. Calcd for $C_{16}H_{34}Si_2$ (282.6): C, 70.92; H, 12.50. Found: C, 70.90; H, 12.39.

Bis(allylsilane) (6e). Yield 56%. Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.45−7.26 (m, 4H, Ph), 5.14 (s, 2H, C=CH_2), 4.88 (s, 2H, C=CH_2), 2.05 (s, 4H, CH_2Si), −0.07 (s, 18H, SiCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 147.2, 143.0, 128.2, 125.6, 124.8, 110.4, 26.6, −1.0. IR (film): ν (cm^{-1}) = 3083, 1617, 1249, 854. Anal. Calcd for $C_{14}H_{30}Si_2$ (254.5): C, 71.44; H, 9.99. Found: C, 71.45; H, 9.95.

Bis(allylsilane) (6f). Yield 65%. White solid: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.34−6.82 (m, 4H, Ph), 5.06 (s, 2H, C=CH_2), 4.78 (s, 2H, C=CH_2), 4.04 (s, 4H, OCH_2), 1.99 (s, 8H, OCH2C*H2*), −0.06 (s, 18H, SiCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 158.7, 146.2, 135.5, 127.8, 114.3, 108.8, 67.7, 26.4, −1.0. IR (KBr): ν (cm^{-1}) = 3088, 1609, 1245, 1057, 837. Anal. Calcd for $C_{28}H_{42}O_2Si_2$ (466.8): C, 72.04; H, 9.07. Found: C, 72.06; H, 9.13.

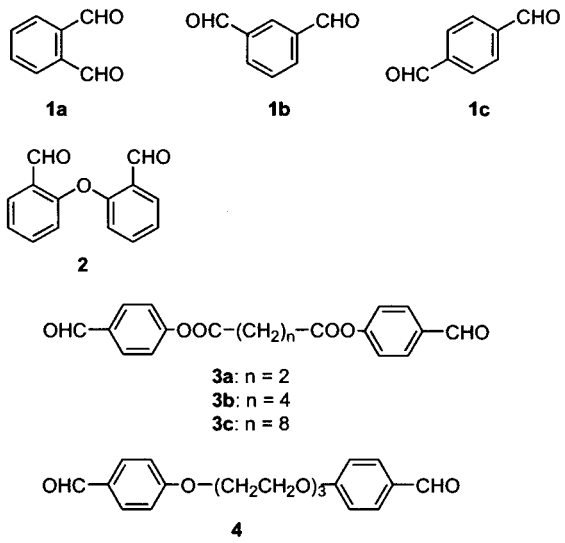
Bis(allylsilane) (6g). Yield 54%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.36−6.87 (m, 4H, Ph), 5.10 (s, 2H, C=CH_2), 4.81 (s, 2H, C=CH_2), 4.12 (m, 4H, PhOCH_2), 3.86 (m, 4H, $PhOCH_2CH_2$), 3.75 (s, 4H, $PhOCH_2CH_2OCH_2$), 2.01 (s, 4H, CH_2Si), −0.06 (s, 18H, SiCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 158.3, 145.8, 135.4, 127.4, 114.2, 76.9, 71.0, 67.4, 26.2, −1.2. IR (KBr): ν (cm^{-1}) = 3086, 1608, 1248, 1059, 844. Anal. Calcd for $C_{30}H_{46}O_4Si_2$ (526.9): C, 68.39; H, 8.80. Found: C, 68.28; H, 8.75.

Model Reaction (1). A solution of (2*R*,3*R*)-2-*O*-(2,6-diisopropoxybenzoyl)tartaric acid (74 mg, 0.2 mmol) and 3,5-bis(trifluoromethyl)phenylboronic acid (51 mg, 0.2 mmol) in dry propionitrile (1 mL) was stirred for 30 min at room temperature under argon to form chiral (acyloxy)borane (**11b**).[12a] After the above solution was cooled to −78 °C, benzaldehyde (106 mg, 1 mmol) and **9b** (190 mg, 1 mmol) were added and stirred for 3 h at −78 °C. The reaction mixture was then poured into brine and extracted with ether, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (hexanes/EtOAc 4:1) to give **10b** as a white solid (222 mg, 99%): ^{1}H NMR ($CDCl_3$) δ 7.49−7.29 (m, 10H, Ph-*H*), 5.44 (br s, 1H, =CH_2), 5.19 (br s, 1H, =CH_2), 4.75 (m, 1H, C*H*OH), 3.05 (m, 2H, =C−CH_2), 2.19 (s, 1H, CHO*H*). ^{13}C NMR ($CDCl_3$): δ 145.3, 144.2, 140.6, 128.7, 128.1, 127.8, 126.6, 126.1, 116.1, 72.3, 46.2; IR (film) 3220, 2940, 1627 cm^{-1}. The enantioselectivity (79% ee) was determined by HPLC analysis using a chiral stationary-phase column (Daicel, Chiralpac AD; hexane/propan-2-ol 30:1; 0.5 mL/min): (*R*)-**10b** t_r = 34.1 min; (*S*)-**10b** t_r = 38.2 min. The homoallyl alcohol **10b** was converted to the know compound (3-hydroxy-1,3-diphenylpropan-1-one) by Lemieux−von Rudloff oxidation,[13] and the absolute configuration was determined to be *R* by comparison of the optical rotation of the corresponding hydroxy ketone with the literature value.[14]

Model Reaction (2). Chiral (acyloxy)borane (**11b)** prepared from (2*R*,3*R*)-2-*O*-(2,6-diisopropoxybenzoyl)tartaric acid (74 mg, 0.2 mmol) and 3,5-bis(trifluoromethyl)phenylboronic acid (51 mg, 0.2 mmol) in dry propionitrile (1 mL) was cooled to −20 °C. Benzaldehyde (106 mg, 1 mmol) and **6d** (151 mg, 0.5 mmol) were added to the above solution and stirred for 1 h. The reaction mixture was then poured into brine and extracted with ether, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (hexanes/EtOAc 2:1) to give diol as a white semisolid (168 mg, 91%): ^{1}H NMR ($CDCl_3$): δ 7.45−7.27 (m, 14H, Ph-*H*), 5.47 (br s, 2H, =CH_2), 5.19 (br s, 2H, =CH_2), 4.75 (m, 2H, C*H*OH), 3.05 (m, 4H, =C−CH_2), 2.19 (s, 2H, CHO*H*). ^{13}C NMR ($CDCl_3$): δ 144.6, 144.2, 139.9, 128.7, 127.9, 126.7, 126.1, 116.1, 72.4, 46.0. IR (film): 3399, 2940, 1623 cm^{-1}. Anal. Calcd for $C_{26}H_{26}O_2$ (370.5): C, 84.29; H, 7.07. Found: C, 84.21; H, 7.13.

Typical Procedure of Asymmetric Polymerization. A typical experimental procedure is described in the following polymerization of **6d** with **3b**. Dry propionitrile (1 mL) solution

Chart 1



of **11b** prepared from (2*R*,3*R*)-2-*O*-(2,6-diisopropoxybenzoyl) tartrate (74 mg, 0.2 mmol) and 3,5-bis(trifluoromethyl)phenylboroic acid (51 mg, 0.2 mmol) was added to a solution of bis(allylsilane) **6d** (151 mg 0.5 mmol) and dialdehyde **3b** (177 mg, 0.5 mmol) in propionitrile (1 mL) at −20 °C. The mixture was stirred at −20 °C for 1 h and quenched with methanol (1 mL) and 1 M TBAF/THF solution (1 mL). The mixture was poured into MeOH/H_2O (2:1), filtered, and dried under vacuum to yield a white solid (289 mg, 99%). Complete removal of **11b** was confirmed by NMR, IR, and TLC.[15] M_n = 14 000, M_w/M_n = 4.64, $[\alpha]_{405}$ −223.2, $[\Phi]_{405}$ −1144.1 (*c* 1.0, THF).[16] ^{1}H NMR ($CDCl_3$): δ 7.39 (4H, Ph-*H*), 7.33 (4H, Ph-*H*), 7.04 (4H, Ph-*H*), 5.43 (2H, C=CH_2), 5.15 (2H, C=CH_2), 4.70 (2H, C*H*OH), 2.90 (4H, =CCH_2), 2.58 (4H, O=CCH_2), 1.85 (4H, O=CCH_2CH_2). ^{13}C NMR ($CDCl_3$): δ 172.6, 150.3, 144.5, 141.7, 139.9, 127.2, 126.7, 121.8, 116.3, 71.9, 46.1, 34.2, 24.5. IR (film): 3495, 2933, 1755, 1645, 1603, 842 cm^{-1}.

Results and Discussion

Monomer Synthesis. We used commercially available dialdehydes (**1**, **2**) and newly synthesized dialdehydes (**3**, **4**) as monomer of the allylation polymerization (Chart 1). Dialdehydes **3** were prepared easily by condensation of 4-hydroxybenzaldehyde with the corresponding dicarboxylic acid chloride. Dialdehyde containing oligo ether linkage **4** was prepared from 4-hydroxybenzaldehyde and triethylene glycol ditosylate.

To obtain bis(allylsilane) as another monomer in high purity, we have tested various reaction conditions to construct the allylsilane moiety. Although metalation of allyl derivatives followed by silylation is a useful method to prepare allylsilane compounds,[17] the diallyl derivatives afforded the desired bis(allylsilane) contaminated with monosilylated compounds which could not be removed by distillation or column chromatography. Palladium-catalyzed arylation of allyltrimethylsilane with aryl triflates[18] gave regioisomeric mixture which could not be purified. We have then applied Narayanan's method of allylsilane synthesis[19] to the preparation of bis(allylsilane)s. In this method, diester was treated with Grignard reagent prepared from chloromethyltrimethylsilane in the presence of $CeCl_3$ to give the diol intermediate **5** as shown in Scheme 1. Usual acidic workup of the diol gave the corresponding bis(allylsilane) **6** contaminated with partly desilylated compounds, which was also difficult to be removed (Table 1, entry 1). However, we found that careful treatment

Scheme 1. Preparation of Bis(allylsilane) Monomer

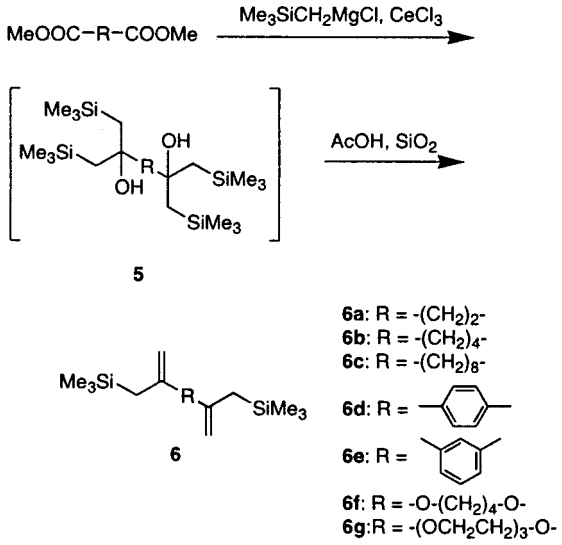
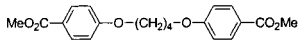
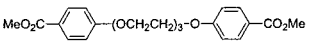


Table 1. Preparation of Bis(allylsilane) Monomer

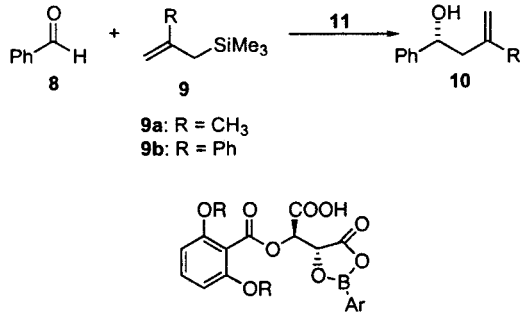
entry	diester	bis (allylsilane)	condition[a]	yield[b] (%)
1	**dimethyl terephthalate**	**6d**	A	54 (+36)[c]
2	**dimethyl terephthalate**	**6d**	B	20
3	**dimethyl terephthalate**	**6d**	C	89
4	**dimethyl isophthalate**	**6e**	C	56
5	**dimethyl sebacate**	**6c**	C	61
6	**dimethyl adipate**	**6b**	C	57
7	**dimethyl succinate**	**6a**	C	60
8		**6f**	C	65
9		**6g**	C	54

[a] A: 1 N HCl aqueous solution, 30 min, rt. B: silica gel, 15 h, rt. C: silica gel + 10% AcOH, 30 min, rt. [b] Isolated, purified yield. [c] Mixture of bis(allylsilane) (54%) and mono(allylsilane) (36%), which could not be separated.

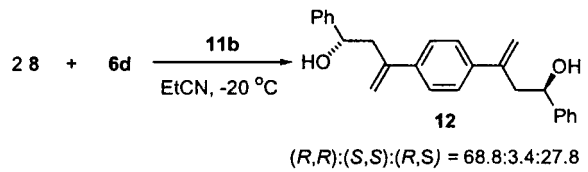
of the diol with acetic acid in the presence of silica gel could suppress the formation of desilylated compounds. In this method, the desired bis(allylsilane)s **6** are isolated in pure form by simple distillation or flush chromatography. Bis(allylsilane)s prepared by this method are shown in Table 1. These bis(allylsilane)s are stable in air and moisture and storable.

Enantioselective Addition of Allylsilane to Benzaldehyde as a Model Reaction. When enantioselective C−C bond forming reaction is applied to the asymmetric polymerization, the reaction should occur in quantitative conversion without any side reaction; otherwise, a chiral polymer having the desired main chain structure with high molecular weight would be difficult to obtain. To confirm whether the above requirement is satisfied in the asymmetric allylation reaction, we have tested an enantioselective addition of β-substituted allyltrimethylsilane **9** to benzaldehyde **8** (Scheme 3). There are several reports on chirally modified Lewis acid catalyst for enantioselective addition of allylsilane to aldehyde.[12] Among them, Yamamoto demonstrated that chiral (acyloxy)borane (CAB) efficiently catalyzed the same type of reactions to give the enantioenriched homoallylic alcohol in quantitative

Scheme 2. Model Reaction (1)



Scheme 3. Model Reaction (2)



(*R*,*R*):(*S*,*S*):(*R*,S) = 68.8:3.4:27.8

Table 2. Model Reaction of Benzaldehyde with β-Substituted Allylsilane 9 in the Presence of CAB 11b

entry	allylsilane	solvent	temp (°C)	time (h)	yield (%)	ee (%)[a]
1	**9a**	C_2H_5CN	−20	1	99	75
2[b]	**9a**	C_2H_5CN	−78	2	99	89
3	**9b**	C_2H_5CN	0	0.5	99	57
4	**9b**	C_2H_5CN	−20	1	99	58
5	**9b**	C_2H_5CN	−78	3	99	79
6	**9b**	THF	−78	5	62[c]	56
7	**9b**	CH_2Cl_2	−78	5	49[d]	60

[a] Determined by chiral HPLC on a Chiralcel OD-H column. [b] Reported in the literature.[12] [c] 30% of benzaldehyde was recovered. [d] 43% of benzaldehyde was recovered.

yield without any side reaction.[12] We believe that CAB is one of the most effective and reliable catalyst for this reaction. As a model reaction of asymmetric polymerization, we examined the enantioselective addition of β-substituted allylsilane **9** to benzaldehyde **8** in the presence of CAB **11b** (Table 2). Without catalyst, no reaction occurred between these substrates. The enantioselective addition was catalyzed with **11b** to give the desired homoallylic alcohol as a single product in quantitative yield. Enantioselectivity of the homoallylic alcohol product was easily determined by means of HPLC equipped with chiral stationary phase column. Enantioselective addition of methallylsilane gave higher selectivity than in the case of β-phenylallylsilane. Although the enantioselectivity at −20 °C was almost the same as that at 0 °C in both substrates, lowering the reaction temperature to −78 °C resulted in higher enantioselectivity as expected. Choice of the solvent in this reaction was propionitrile.

An additional model reaction of bis(allylsilane) **6d** with **8** would lead to a more reliable estimation of the asymmetric induction degree of polymerization. As shown in Scheme 4, the asymmetric reaction between 2 equiv of **8** and 1 equiv of **6d** took place smoothly at −20 °C in the presence of **11b** to give chiral diol **12** in quantitative conversion. HPLC analysis of **12**[20] indicated a ratio of 68.8:3.4:27.8 for the stereoisomers (*R*,*R*)-

Scheme 4. Asymmetric Allylation Polymerization

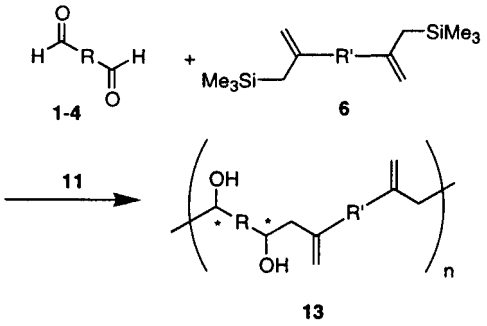


Table 3. Asymmetric Allylation Polymerization of Dialdehyde 3b with Bis(allylsilane) in the Presence of 11b at −20 °C

entry	bis(allyl-silane)	time (h)	yield (%)[a]	M_n[b]	M_w/M_n[b]	$[\alpha]_{405}$[c]	$[\Phi]_{405}$[d]
1	**6a**	72	87	4300	3.04	+37.2	+149.0
2	**6b**	72	96	7400	3.07	+37.5	+184.7
3[e]	**6b**	1	92	6800	3.58	+15.5	+76.4
4[f]	**6b**	1	89	5100	4.01	+6.4	+31.5
5[g]	**6b**	3	78	5500	11.83	+9.4	+46.3
6[h]	**6b**	1	82	5400	6.52	+17.0	+83.7
7[i]	**6b**	4	88	7800	4.53	+34.2	+168.5
8	**6c**	24	90	9300	5.43	+34.3	+188.2
9	**6d**	1	99	14000	4.62	−223.2	−1144.1
10	**6e**	2	69	9300	2.24	−76.0	−389.3
11[j]	**6f**	24	0				
12	**6g**	1	85	4200	4.98	−93.4	−688.3

[a] Isolated polymer yield after removal of CAB. [b] Determined by SEC calibration using polystyrene standards in THF solution. [c] Specific rotation value measured in THF. [d] Molar rotation value measured in THF. [e] At room temperature. [f] **11a** was used at room temperature. [g] **11c** was used at room temperature. [h] **11d** was used at room temperature. [i] **11d** was used at −20 °C. [j] **6f** was insoluble in propionitrile, and no reaction occurred with dialdehyde.

12, (*S*,*S*)-**12**, and (*R*,*S*)-**12**, which is roughly consistent with the result obtained from the model reaction of **8** and **9** in Scheme 3. The model reactions mentioned above revealed that this reaction using CAB can be applied to the asymmetric allylation polymerization.

Asymmetric Allylation Polymerization. The above-mentioned model reaction study encouraged us to apply the asymmetric allylation reaction to the chiral polymer synthesis (Scheme 4). Table 3 showed the asymmetric allylation polymerization of dialdehyde **3b** and various bis(allylsilane)s. CAB **11b** initiated the asymmetric polymerization of **3b** and **6** in propionitrile at −20 °C. The monomers were completely consumed in the polymerization to give the chiral polymer, which was poured into methanol/water to precipitate. Polymers precipitated in methanol/water were isolated by filtration. This procedure provided complete removal of **11b** although a small amount of polymers were lost during this process in some cases. THF solution of the chiral polymer **13** obtained by this method showed optical activity. Chiral polymers obtained from aliphatic bis(allylsilane)s showed positive rotation values, while aromatic ones gave negative values. In the case of **6f**, its very low solubility in the solvent completely prevented the polymerization. In comparison with **11b**, the dimethoxy derivative **11a** yielded a polymer with a somewhat lower molar optical rotation (entries 3 and 4). This result is consistent with Yamamoto's report that **11b** is a more efficient catalyst than **11a** for the enantioselective allylation of aldehyde.[12] The pentafluorophenyl derivatives **11c** and **11d** also catalyzed the same polymerization to give the optically active polymers (entries 5−7). These catalysts showed higher molar optical rotation as compared to **11a**.

Table 4. Asymmetric Allylation Polymerization of Various Dialdehyde with Bis(allylsilane) 6d at −20 °C

entry	dialde-hyde	time (h)	yield (%)	M_n[a]	M_w/M_n[a]	$[\alpha]_{405}$[b]	$[\Phi]_{405}$[c]
1	**1a**	2	98	1000	4.58	+120.9	+353.5
2	**1b**	2	70	5400	1.97	−225.4	−659.1
3	**1c**	2	83	3600	3.62	−323.5	−945.8
4	**2**	4	93	1400	4.00	−38.3	−147.2
5	**3a**	1	93	14000	9.23	−210.0	−1016.9
6	**3b**	1	99	14000	4.62	−223.2	−1141.1
7[d]	**3c**	0.5	88 (60)[e]	9900	3.04	−103.7	−589.6
8	**3c**	1	96	23000	4.64	−177.6	−1010.1
9[f]	**3c**	6	89	11000	6.45	−194.9	−1108.5
10	**4**	2	91 (75)[e]	6600	4.17	−136.5	−705.3

[a] Determined by SEC calibration using polystyrene standards in THF solution. [b] Specific rotation value measured in THF. [c] Molar rotation value measured in THF. [d] At 0 °C. [e] THF-soluble part. [f] At −78 °C.

Of bis(allylsilane)s used, **6d** showed relatively higher reactivity. The chiral polymers having higher molecular weight with large optical rotation value were obtained using **6d**. Thus, in Table 4, **6d** was allowed to react with other dialdehyde monomers using **11b**. Within a few hours at −20 °C, chiral polymer was yielded in all cases. Dialdehydes **1** and **2** gave polymers having low molecular weight. However, asymmetric polymerization of **3** resulted in higher molecular weight with large molar optical rotation values. In most cases, insufficient solubility of dialdehydes in propionitrile prevented the asymmetric polymerization at the temperature below −20 °C. We have found that **3c** having long alkyl chain showed better solubility even at −78 °C in propionitrile and produced chiral polymer (entry 9), although somewhat longer reaction time was required. The same monomer was also polymerized with **6d** very rapidly at 0 °C to give the polymer containing THF insoluble part (entry 7). Another dialdehyde monomer **4** gave the chiral polymer, which also contained some THF-insoluble material.

Conclusion

We described a novel polymerization chemistry based on Sakurai−Hosomi allylation reaction. This C−C bond forming reaction can be repeated between dialdehyde and bis(allylsilane) to yield the polymer containing unique main chain structure of exo methylene and secondary alcohol. Chiral (acyloxy)borane as a chiral Lewis acid catalyst promoted the asymmetric allylation polymerization to give the optically active polymers in high yield. A model reaction study revealed that the asymmetric polymerization proceeded in a stereoselective manner. The ability to prepare optically active polymers using asymmetric allylation reaction may prove useful in a variety of chiral polymers applications. Other asymmetric C−C bond forming reactions can be utilized for the preparation of novel chiral polymers.

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Supporting Information Available: Experimental procedures for compounds **3c** and **6c** and HPLC data for compound **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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